

**Final Report**

**Environmentally Acceptable Photoresist Processing  
for Integrated Circuit Manufacture  
Contract N00014-94-C-0235**



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**19951012 043**

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## 1.0 INTRODUCTION

This is the final report of work carried out on Contract No. N00014-94-C-0235, Environmentally Acceptable Photoresist Processing for Integrated Circuit Manufacture.

During the final work period an investigation of supercritical carbon dioxide (SC CO<sub>2</sub>) developing to produce negative images with traditionally positive resists was carried out. Compositional effects on solubility of the modified polymer systems described in the second bimonthly report (of 26 January) were studied in more detail, and exposure and imaging studies were carried out with one of the polymer systems - a fluoromethacrylate/t-butyl methacrylate copolymer.

This report describes the overall program results including those presented in the first and second bimonthly reports. Background information on supercritical fluid (SCF) technology and photoresist developing is included.

### 1.1 Significance and Impact of Phase I

Manufacture of integrated circuits is undergoing continual evolution toward smaller circuitry and faster information processing. Optical lithography is the most widely used, most versatile, fastest, and least expensive exposure technology in existence. Currently, I-line (365nm) and deep ultraviolet (DUV or 248nm) lithography are employed to achieve 0.5 $\mu$  features using novolak and hydroxystyrene photoresists, respectively. However, these technologies have nearly reached the limit of their capabilities, and shorter wavelengths and/or new resists will be required to achieve smaller geometries. 193nm technology represents the most promising candidate for meeting the requirements of next-generation semiconductors. In order to bring this technology to commercial reality, while meeting the increasingly stringent environmental requirements, appropriate photoresists and next-generation developing techniques will be necessary. This Phase I effort has provided the opportunity to investigate both.

The evolution of the electronics industry was described in a plenary lecture made at a recent International Symposium on Microlithography sponsored by The International Society for Optical Engineering (Santa Clara, CA, Feb. 19-24, 1995). Ms. Karen Brown, Director of Lithography of SEMATECH, a consortium composed of members from industry, government, and academia involved in electronics and semiconductor manufacturing, presented the needs and challenges facing the electronics industry for the next decade. Several points of her lecture bear repeating, especially for their relevance and importance to a Phase II program:

- Semiconductor manufacturers desire to continue using optical lithography as long as possible.
- Electron-beam and x-ray lithography represent much higher investment and risk (than optical).
- Feature size (of images) is predicted to be reduced from the current 0.5 $\mu$  to 0.07 $\mu$  over the next 10-15 years; the near-term goal is 0.18 $\mu$ .
- In order to maintain increasing performance demands, 25-30% improvement per year

must be made including smaller features, increased yield, and higher productivity.

- The biggest issues concern environmental aspects, health and safety, and a "total system" approach.
- Over \$400 million per year is spent in the United States for development of lithographic technology.
- It is estimated that \$243-\$363 million will be spent over the next five years for solely process development and prototype equipment for 193nm lithography for generating 0.18 $\mu$  features; \$97 million represents anticipated costs for development of next-generation resists alone.
- Currently, total wafer processing costs are \$4/cm<sup>2</sup> with the lithography cost alone representing \$1.50/cm<sup>2</sup>. Projected lithography cost by year 2000 is \$2.50/cm<sup>2</sup>.

Ms. Brown further pointed out the need for "greatly increased emphasis and resources on 193nm technology to bring it to pilot production in 1998 for the 0.18 $\mu$  generation".

IBM, and particularly their Almaden Research Center in San Jose, has historically maintained a strategic position in photoresist technology and plans to establish a strong early development and manufacturing position for 0.18 $\mu$  feature lithography at 193nm. The efforts on this Phase I program have been greatly influenced by the needs and challenges of the electronics industry and complement the ongoing efforts at IBM and MIT Lincoln Laboratory (Lexington, MA); both groups have expressed interest in continuing a cooperative effort with Phasex. At this stage of research and process development, however, the SC CO<sub>2</sub> developing process is still considered too high risk for IBM (and most companies) to make the significant investment necessary for full-scale development. If some of the remaining technical and economic issues are more thoroughly investigated, industry would be more likely to consider Phase III investment.

The accomplishments on this Phase I program have generated considerable interest within IBM. Since the year 2000 is the target date for commercial, full-scale production of semiconductors using 193nm technology, this project comes at an opportune moment to establish a foothold in that area. The novel resist systems investigated in combination with the SC CO<sub>2</sub> developing process on this program lend themselves readily to 193nm technology, and the opportunity to introduce them into next-generation manufacturing is enormous.

Recent activities at IBM have demonstrated that negative photoresist processes for production of certain critical levels in the integrated circuit result in significant improvements in microchip performance. To date there have not been any reports in the scientific or patent literature of 193nm negative tone photoresists. As feature size becomes increasingly smaller, significant problems with liquid developers such as swelling and resist pattern collapse (caused by the surface tension of liquids) arise. SC CO<sub>2</sub> developing of photoresists can eliminate these problems in addition to reducing the waste associated with traditional developing processes. Used in conjunction with next-generation negative resists, and with positive resists as well, the SC CO<sub>2</sub> developing process offers an environmentally conscious and potentially superior method for achieving the next-generation goals of the electronics industry.

## **1.2 Program Objectives**

The primary objective of this Phase I program was to demonstrate that SC CO<sub>2</sub> technology is a technically feasible alternative to solvent methods for photoresist developing, and that this new "dry" developing technique could be applied to a variety of polymeric photoresists. As will be presented in this report, both objectives have been achieved. The motivations for carrying out this work involves both environmental issues concerning photoresist processing, and improvements in product quality and performance to achieve next-generation specifications. In addition to meeting the environmental requirements, a number of novel photoresists have been generated that are potential candidates for 193nm lithography and that will be useful for both single layer and bilayer applications; these materials are being designed specifically for use with SC CO<sub>2</sub> developing.

Other Phase I technical objectives involved comparison between conventional solvent developing and SC CO<sub>2</sub> developing processes in terms of environmental and waste issues and performance, i.e., image quality. Some preliminary costs and a commercialization plan are discussed as well. Although these other objectives are addressed, significantly more effort was directed toward the technical aspects of the program.

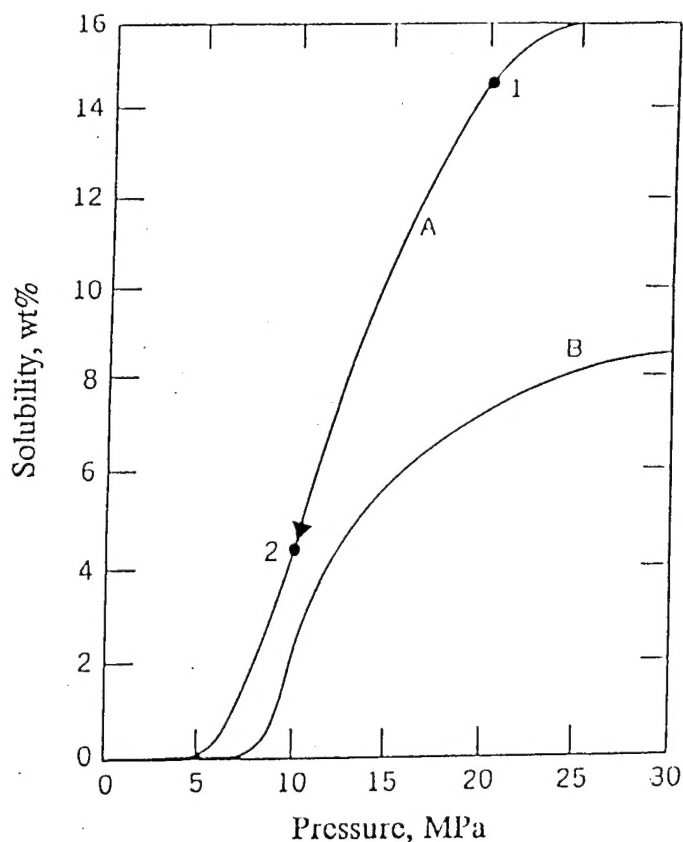
## **2.0 BACKGROUND**

### **2.1 Supercritical Fluids**

Supercritical fluids have been used for two decades now in the processing of coffee, tea, spices, hops, and other foods and beverages to produce improved and solvent-free products.<sup>1-3</sup> Although in the late 70s to the mid 80s SCFs were proposed for many ill-advised applications, including low energy separations processes (to replace distillation), regeneration of activated carbon, and "degreasing" potato chips and other snack foods, on the positive side, today SCFs are receiving resurgent attention for specific opportunities. The combination of current successes and proliferating knowledge of the operation of large industrial processes have pointed out that supercritical fluid extraction is not (just) a laboratory curiosity but a viable, scaleable industrial process.

The application of SCFs to photoresist developing exploits the pressure dependent solubility characteristics of dense gases, for selectively dissolving soluble portions of the exposed resist. Supercritical carbon dioxide (SC CO<sub>2</sub>) is most useful for this particular application because of its environmental advantages over liquid solvents. The tremendous selectivity of SCF developers can minimize or eliminate the swelling problems associated with liquid developers and may lead to improved contrast or resolution. Furthermore, use of a dense gas offers the potential to eliminate resist pattern collapse which arises due to surface tension effects of liquid developers,<sup>4</sup> and could be especially useful in producing sub-half micron images which is the goal for next generation semiconductors.

The phenomenon of SCF solubility was first reported over one hundred years ago by Hannay and Hogarth.<sup>5</sup> As a demonstration of the pressure dependent dissolving power of SCF solvents, Figure 1 shows the solubility of a simple compound, naphthalene, in carbon dioxide and ethylene.<sup>6</sup>

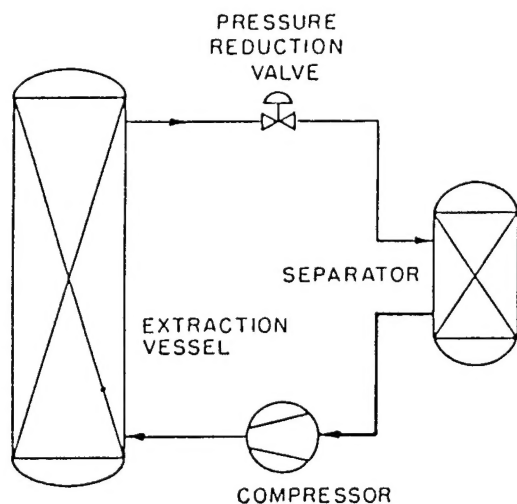


**Figure 1. Solubility Data of Naphthalene in Ethylene (A) and Carbon Dioxide (B)**

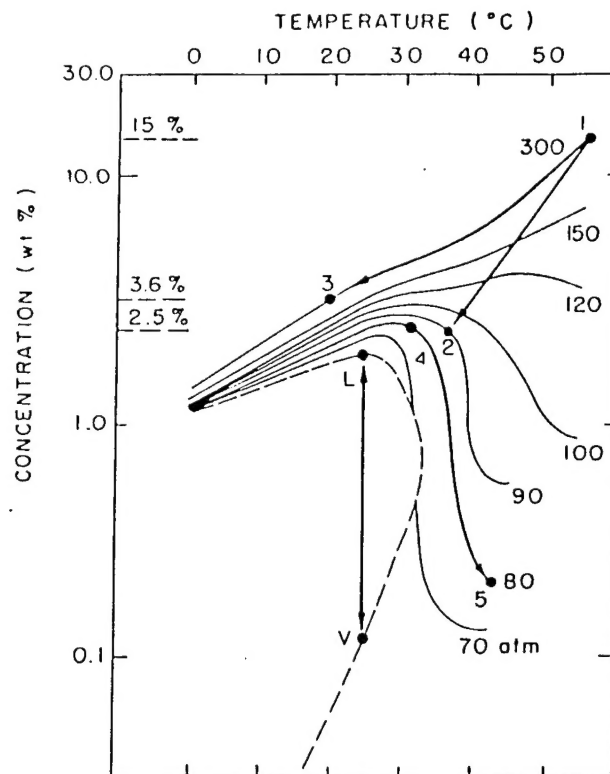
Above the critical pressure of each gas, 50 atm for ethylene and 73 atm for carbon dioxide, it is seen that increases in pressure result in large increases in solubility of naphthalene. Because of such dissolving characteristics, it is possible to design industrial processes to extract, purify, and fractionate materials based on changes in pressure of a supercritical fluid solvent.<sup>7</sup> At high pressure an extraction can be carried out, for example at Point 1 on the ethylene solubility curve and by lowering the pressure to Point 2 a separation of the dissolved material from the gas can be made to occur; the solvent can then be recycled to the extractor to carry out more extraction.

A schematic diagram of a batch process which uses a supercritical fluid as a pressure-dependent solvent to extract an organic substance is given in Figure 2a.<sup>8</sup> Four basic elements of the process are shown, viz., an extraction vessel, a pressure reduction valve, a separator for collecting the material dissolved in the extractor, and a compressor for recompressing and recycling the gas. (Control and measurement functions and heat exchange equipment are omitted from the figure for clarity and ease of presentation.) Figure 2b shows extensive data on the solubility of naphthalene in carbon dioxide as a function of temperature and pressure.<sup>9</sup>





**Figure 2a. Extraction Process Operation**



**Figure 2b. Solubility Behavior**

Reference to Figures 2a and 2b is made in explaining how a supercritical fluid process operates. Some process operating parameters are indicated on two solubility isobars in Figure 2b: Point 1 represents conditions in the extractor, e.g., 300 atm, 55°C, and Point 2 the conditions which exist in the separator, 90 atm, 32°C. The extractor vessel is assumed to be filled with naphthalene in admixture with other materials which for purposes of this discussion are assumed to be insoluble in carbon dioxide. Carbon dioxide (at the conditions of Point 1) is passed through the extraction vessel wherein it dissolves (and extracts) the naphthalene from the insoluble material. The carbon dioxide dissolves the naphthalene to a concentration of 15%, and the solution leaving the extractor is expanded to 90 atm through the pressure reduction valve as indicated by the directed path 1-2 in Figure 2b. During the pressure reduction step, naphthalene precipitates from the solution because as Figures 1 and 2b show, the dissolving power of carbon dioxide is lowered when the pressure is decreased. The precipitated naphthalene is collected in the separator, the gas is recompressed and returned to the extractor, and this recycle process continues until all the naphthalene is dissolved and extracted, the directed line segment 1-2 in Figure 2b and its reverse on the solubility diagram representing approximately the cyclic process. (The other directed lines designate other operating modes, and it is pointed out that the dissolving power of a supercritical fluids is both pressure dependent and temperature dependent.) The developing of photoresists would operate in essentially the same manner; the gas would selectively dissolve the soluble portions of the exposed pattern, leaving the insoluble polymer behind.

Even though the solubility data for naphthalene dissolved by carbon dioxide have been used to explain the operation of a supercritical fluid process, the solubility behavior shown in Figure 2b is very general, applying to any solid material (and many liquid materials) that dissolve to a modest extent in any supercritical fluid; many gas-solute systems have been presented in the literature<sup>1</sup>, and the differences among various materials is only one of degree, e.g., the solubility of some other material in carbon dioxide may be higher or lower than that of naphthalene, but the pressure-temperature-concentration curves will exhibit similar characteristics. Thus, the extraction process described is quite general for many materials.

In addition to the unique pressure-dependent dissolving properties of SCF solvents, it was related that supercritical fluids exhibit very attractive transport properties. Table 1 compares the diffusivity, viscosity, surface tension, and density of typical organic solvents such as hexane and toluene to typical supercritical solvents like carbon dioxide and ethylene.

**Table 1. Comparison of Properties of Supercritical Fluids and Organic Solvents**

<u>Solvent</u>	<u>Diffusivity</u> (cm <sup>2</sup> /sec)	<u>Viscosity</u> (cps)	<u>Density</u> (g/cc)	<u>Surface Tension</u> (dynes/cm)
Supercritical Fluid	10 <sup>-3</sup>	0.02-0.05	0.6-1.0	0
Organic	10 <sup>-5</sup>	1	0.8	20-50

As the table shows, the diffusivity of a solute diffusing through a supercritical fluid is two orders of magnitude higher than in a liquid solvent; a high diffusivity equates to high extraction rates of a component from liquid and solid surfaces. The viscosity of a supercritical fluid is much, much lower than that of a liquid, and a low viscosity and a zero surface tension (zero because there is no gas-liquid interface) make possible the extraction of materials from pores and cell structures with dimensions of less than one micron. The zero surface tension also is important for the reverse of extraction, viz., infiltration of materials into small pores. Supercritical fluid solvents have the ability to penetrate into pores and channels of dimensions much less than one micron, and supercritical fluids can also dissolve in a wide range of polymers and lower their glass transition temperatures temporarily while the polymer is under the action of the supercritical fluid.<sup>10,11</sup> Since in the lithographic procedure the masking and exposure operations produce extremely small patterns and intricate geometries, these latter properties of SCFs may offer significant advantages over liquid developers, including ion-free development, greater process latitude and improved pattern definition.

Applications of SCF technology are quite diverse, ranging from extraction and fractionation to more complex operations such as infiltration/deposition,<sup>12</sup> recrystallization,<sup>13,14</sup> and surface modification,<sup>15</sup> and it has even been applied as an alternative to CFC-113 (and other hazardous solvents) for delicate parts cleaning.<sup>16</sup> Of relevance to photoresist developing are applications to polymer systems. Several examples are listed below (which represent research carried out at Phasex) that demonstrate the breadth of experience with polymers.

- fractionation of reactively terminated polysiloxanes (for fundamental studies),<sup>17</sup>
- fractionation of energetic propellant binders (for properties improvement),<sup>18</sup>
- purification of polymeric substitute blood surfactant (for decreased toxicity),<sup>19</sup>
- extraction of perfluoropolyether lubricant (for volatility control),<sup>20</sup>

- fractionation of high crystallinity polyethylene (for fundamental studies),<sup>21</sup> and
- fractionation of liquid crystal polymers<sup>22</sup> (for reduction of transition temperature range).

The solubility of polymers (and many oils) in SCFs is more complex than for simple compounds because of the wide molecular weight distribution. However, polymers can be fractionated by molecular weight by taking advantage of the pressure dependent solubility characteristics of SCFs; fractionation is carried out using, for example, an increasing pressure profile.<sup>23</sup> The fractions that are obtained typically show a monotonic increase in molecular weight proportional to the pressure as is discussed in a paper on novolak photoresist fractionation that was presented at the same Microlithography Symposium previously discussed<sup>24</sup>. As an example of the separation capabilities of supercritical CO<sub>2</sub>, a high molecular weight silicone oil ( $M_w = 90,000$ ) was fractionated<sup>25</sup>; Table 2 gives the molecular weight values of the parent silicone and of the supercritical fluid fractions. Each cut was obtained using increasingly higher pressure levels (ranging from 120 atm to 374 atm) and was analyzed by gel permeation chromatography. For photoresist developing it is crucial to operate in a pressure/temperature region where even the highest molecular weight species are soluble, and simultaneously where the lowest molecular weight species of the image-forming polymer is insoluble. This selective dissolution is readily achievable given the nature of lithography: after exposure the exposed and unexposed portions of the film exhibit very different solubilities in the same solvent.

**Table 2. Molecular Weight of Silicone Oil Fractionated with Supercritical Carbon Dioxide**

Fraction	Mn	Mw	% of Parent
Parent	42,500	90,000	100
1	428	789	4.0
2	3,310	11,500	5.1
3	27,100	53,200	27.7
4	43,100	57,500	27.9
5	58,900	91,500	28.3
6	112,600	149,900	7.0

During the concentrated effort carried out on polymers processing with supercritical fluids many other types of operations have been identified, e.g., formation of polymer foams and blends<sup>26</sup>, modification of polymer surfaces<sup>15</sup> (to render, for example, a hydrophobic surface hydrophilic), insertion of molecular moieties into polymer films.<sup>27</sup> Experience with these adaptations to the basic extraction process contributes to the knowledge base which has been brought to bear on this project.

## 2.2 Photoresist Developing

The properties of SCFs described in the previous section, lend themselves quite readily to the application of these fluids as photoresist developers. Carbon dioxide, one of the most widely used and accepted SCFs, is a particularly advantageous alternative to liquid developers because of its environmental attributes; it is non-ozone depleting, non-toxic, non-flammable, and "worker friendly".

A central operation in integrated circuit manufacture is lithography, the process by which images or patterns are created on semiconductor wafers. Most prevalent today is the use of radiation or light (photolithography) as the imaging tool, although other more costly and complex methods such as electron-beam and x-ray lithography are used occasionally to achieve certain critical feature levels. Photoresists are polymeric materials which are designed to undergo some chemical change upon exposure to certain wavelengths of light. These resists are classified as positive or negative depending upon their behavior in the developer.

In summary of the photolithographic process, a substrate (typically a silicon wafer) is coated with a thin film of photoresist, exposed through a mask to radiation which induces the chemical change in the exposed areas, then developed to dissolve and remove select portions of the resist. Bilayer and multilayer resist systems, which are composed of one or more layers under the photoresist, are etched after developing. The photoresist patterns provide a protective (or resistant) covering during subsequent processing of select areas of the substrate. Figure 3 is a schematic representation of the photolithographic process for a bilayer system. It is pointed out that the type of images produced after exposure and developing are a function of the polymer system and developer, i.e., positive images are produced when the exposed portions are more soluble in the developer, and negative images are produced when the unexposed portions are more soluble.

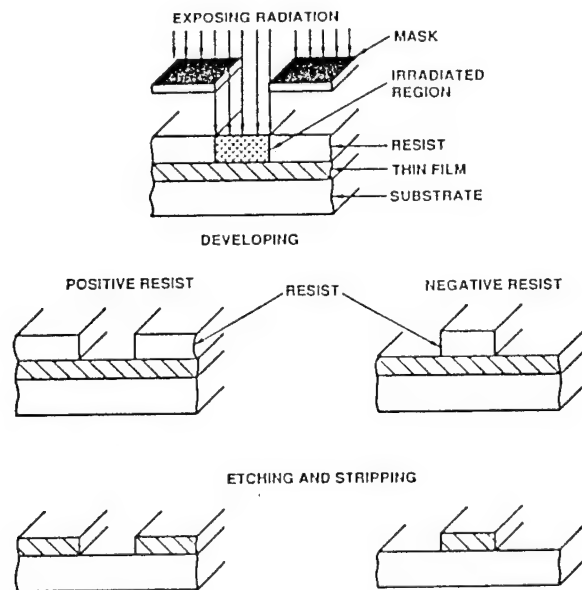


Figure 3. Schematic Diagram of Photolithographic Process

### 3.0 METHODOLOGY

The initial approach on the Phase I program was to apply SC CO<sub>2</sub> developing to silicon-based photoresists, particularly those that can be used with 193nm lithography which is viewed as a primary candidate exposure tool for producing sub-half micron features. The Phase I proposal included a preliminary result which demonstrated proof-of-concept. That system was a polysilane (positive) bilayer resist which was developed via SC CO<sub>2</sub>. It was proposed to investigate silicon-containing resist systems in greater detail for several reasons:

1. Silicon provides an excellent etch barrier making the resist suitable for bilayer and multilayer applications,
2. Upon exposure, polysilanes are converted to polysiloxanes which are generally soluble in SC CO<sub>2</sub> (depending on composition and molecular weight); a positive image would be produced on developing.
3. Polysiloxanes can be used to produce negative images with SC CO<sub>2</sub> developing (the exposure chemistry would be different than that of polysilanes),
4. In order to provide suitable etch resistance in bilayer systems, significant amounts of silicon-containing polymer must be used; the resulting resist and/or exposure products are impossible to develop with aqueous base developers, and instead flammable solvents are required, and
5. Silicon-containing polymers are amenable to 193nm exposure tools.

During the first two months of the program, significant effort was directed toward investigating polysilane resists of varying composition and the effectiveness of SC CO<sub>2</sub> developing. In addition, several potential single layer negative resist systems were examined.

Although silicon-containing resists are useful in lithographic operations, discussions with IBM personnel (Almaden Research Center, San Jose) under subcontract revealed that these resists are of less commercial interest as next-generation resists than, for example, methacrylate-based and styrene-based photoresists. These materials are typically used to produce positive images and are used primarily in single layer systems. Thus, the program was shifted to investigate SC CO<sub>2</sub> developing of these materials but in an entirely new way: as negative resists.

Recent activities at IBM have demonstrated significantly improved microchip performance with the use of negative tone resists for the production of certain critical levels in the integrated circuit. This provided further motivation for studying the ability of SC CO<sub>2</sub> to develop negative images using traditionally positive resists, especially the methacrylates which can be used with 193nm lithography. Since the methacrylate and styrene resist chemistry is based on a polarity change (i.e., an increase in polarity) upon exposure, the concept of replacing the conventional polar solvents (which dissolve the exposed regions to produce positive images) with SC CO<sub>2</sub>, a non-polar solvent, was a viable means of producing negative images (by dissolving the unexposed regions). Furthermore, polymers which undergo cross-linking upon exposure would be amenable to the concept as well.

Some polymers are more suited for application in bilayer systems than in single layer systems, particularly silicon-containing polymers which have "built-in" etch resistance. Bilayer systems require a much thinner layer of photoresist (10x thinner) than single layer systems; a thinner imaging layer translates to a better and smaller image, and generally, lower exposure doses are required to induce the appropriate chemical changes. One of the biggest draw-backs, however, with silicon-containing bilayer resists is that flammable solvents such as isopropyl alcohol are required for the developing step. SC CO<sub>2</sub> is very amenable to dissolving these polymers, and can provide a superior alternative. The best case scenario, then, is a siloxane-containing methacrylate; the methacrylate provides 193nm processability, the silicon provides etch resistance, and SC CO<sub>2</sub> will dissolve the unexposed polymer. This combination offers a promising new resist system and developer for creating negative images with bilayer systems.

### **3.1 Experimental Approach**

The proposed developing concept required a delicate balance between SC CO<sub>2</sub> solubility properties and imaging characteristics of the photoresist. Two solubility requirements essential to the proposed concept of producing negative images are:

1. Prior to exposure, the photoresist must be completely soluble in SC CO<sub>2</sub> at some pressure and temperature conditions, and
2. After exposure, the exposed portions must be completely insoluble in SC CO<sub>2</sub> at the same conditions.

Additionally, the photoresists must possess good imaging characteristics (such as sensitivity, adhesion, and optical transparency), the exposure dose must induce a chemical change sufficient to render the exposed film insoluble in the SC CO<sub>2</sub>, and, finally, the SC CO<sub>2</sub> developing process must selectively dissolve the unexposed portions of the film without damage to the remaining film. The selectivity of SC CO<sub>2</sub> makes it quite suited for carrying out effective developing.

Polymeric resists which undergo polarity change upon exposure include acrylic polymers (acrylates and methacrylates) and styrenic polymers. Based on prior experience with these polymers it is known that they are not readily soluble in SC CO<sub>2</sub>. However, the approach to the opportunity is to incorporate a CO<sub>2</sub>-soluble group such as fluorine or siloxane into the polymer to enhance solubility of the base polymers. Incorporation of siloxane, for example, would make the polymers suitable for use in bilayer systems, and fluorine can enhance sensitivity. One way of incorporating these molecules is to react them directly into the main chain of the polymer; another method is to copolymerize two distinct polymers, one of which contains the CO<sub>2</sub>-soluble group. Both methods were investigated on this program, and it was found that copolymerization provided a more versatile method of varying composition. It would eventually be important to determine the minimum amount of incorporation required to render the unexposed polymer soluble in SC CO<sub>2</sub> in order to maintain optical transparency, absorbance and other imaging properties.

The experimental approach required many steps before finally producing an image. The polymers were synthesized (or otherwise acquired) and spin-coated onto silicon wafers. SC CO<sub>2</sub> processing was then carried out at several combinations of temperature and pressure with these

unexposed wafers. The objective here was to determine processing conditions which resulted in complete dissolution of the films. Next, another set of wafers as prepared with one of the resist systems and fully exposed, each wafer to a different exposure dose, and SC CO<sub>2</sub> processing was carried out at several conditions. The objective was to determine the exposure dose required to induce sufficient chemical change to render the film completely insoluble, and simultaneously the SC CO<sub>2</sub> conditions. It was important that the SC CO<sub>2</sub> conditions, which previously dissolved the unexposed resist, not dissolve the exposed resist because the later developing tests would require this selective dissolution. Finally, after determining the appropriate SC CO<sub>2</sub> conditions and exposure dose, coated wafers were exposed through a mask then developed by SC CO<sub>2</sub> to produce negative images. At this preliminary stage in the imaging study it was not yet an objective to produce sub-half micron features. Thus, 254nm lithography was used to carry out the exposure as it is well understood and the equipment is readily available. Future imaging studies will utilize 193nm lithography using equipment available at MIT Lincoln Laboratory. (Incidentally, the SC CO<sub>2</sub> developed images shown in the Phase I proposal were generated with 193nm lithography.)

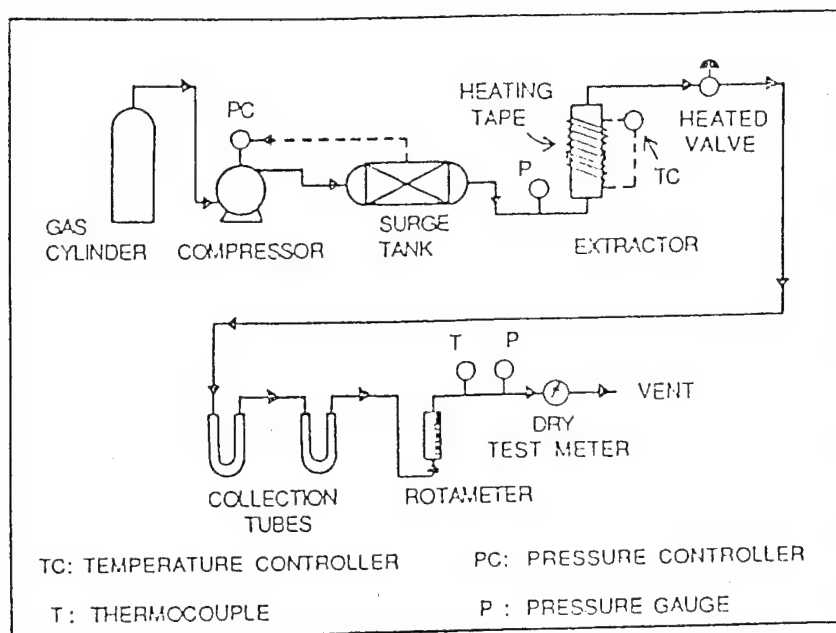
### **3.2 Experimental Procedure**

Test wafers (4" or 1") were prepared at IBM (San Jose) by spin-coating silicon wafers with selected resist solutions and baking. For the preliminary testing with the negative resist systems, no exposure of the wafers was carried out as the first objective was to determine if the unexposed film could be completely dissolved with SC CO<sub>2</sub>. Subsequent tests with negative resists involved exposure of the entire wafers at various exposure doses to examine the exposure/solubility relationship as a function of SC CO<sub>2</sub> conditions, and finally several wafers were exposed through large feature masks to determine the ability of SC CO<sub>2</sub> to selectively dissolve the unexposed portions of the wafers.

The SC CO<sub>2</sub> developing experiments were carried out at Phasex using a standard high pressure extraction system designed and assembled by Phasex; all parts of the system are of 316 stainless steel construction. In order to minimize process time and maximize the amount of information obtained in any single test a relatively small volume cylindrical chamber was used (0.68" ID x 10"). The wafers were sectioned to fit into the chamber and in all experiments several test pieces were processed simultaneously.

Figure 4 is a simple schematic diagram of the test apparatus showing the major components. In operation of the equipment, the sectioned wafers are loosely wrapped with low linting cloth and placed lengthwise into the chamber. After sealing the chamber SC CO<sub>2</sub> at selected temperature and pressure is passed through the system; the flow rate is controlled manually at the pressure reduction valve. As the gas passes through the chamber, soluble portions of the film are dissolved; when the gas pressure is lowered at the pressure reduction valve, the dissolved material precipitates and is collected. After passing a select amount of gas through the vessel, the inlet valve is closed and the chamber is allowed to empty gradually. The test pieces are removed from the chamber, etched (if necessary), and examined.

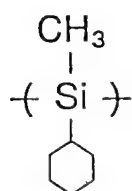




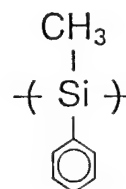
**Figure 4. Schematic Diagram of SC CO<sub>2</sub> Developing Apparatus**

**3.2.1 Positive resists.** One photoresist investigated in the early testing was poly (phenyl methyl) silane (PPMS) the same polymer that was used for the proof-of-concept demonstration described in the Phase I proposal. (Note: in the first bimonthly report this polymer was incorrectly called PMPS.) This time for a bilayer application the PPMS was unsensitized.<sup>30</sup> The sample was prepared as a bilayer system composed of an  $0.08\mu$  PPMS layer on a hard-baked novolak underlayer, and a second sample was prepared with a single  $0.80\mu$  layer of sensitized PPMS on the silicon wafer. Another bilayer system was prepared using unsensitized poly (cyclohexyl methyl) silane on a novolak underlayer for comparing the effects of the pendant group on solubility. Figure 5 shows the chemical structure of the repeating units for these two polymers. The coated wafers were exposed and then developed using SC CO<sub>2</sub> at two sets of conditions summarized in Table 3 (refer to Results section for developing conditions). All of the samples were processed using the same mass (540g) and flow rate ( $\sim 10$  to 15 standard liters per minute, SLPM) of SC CO<sub>2</sub>. The bilayer samples were etched after developing and were evaluated by scanning electron microscopy (SEM) to observe the effectiveness of the CO<sub>2</sub> process.





Poly (cyclohexyl methyl silane) (PCHMS)



Poly (phenyl methyl silane) (PPMS)

Figure 5. Chemical Structure of Repeating Units for Positive Tone Photoresists used in Bilayer Systems.

Table 3. SC CO<sub>2</sub> Conditions for Wafer Developing (Positive Bilayer Resist Systems)

Polymer	T (°C)	Pressure (psi)	CO <sub>2</sub> (grams)
PCHMS	50	3200	540
	80	5600	540
PPMS (sensitized)	50	3200	540
	80	5600	540

**3.2.2 Negative resists.** A variety of polymers were synthesized or obtained for studying the ability of SC CO<sub>2</sub> to produce negative images. (Table 4 shows the structures of repeating units for the various categories of polymers investigated.) All of the polymers were of low to moderate molecular weight and of low glass transition temperature. For the most part, the polymers selected or designed would undergo a polarity change (i.e., polarity increase) during exposure. In addition to the polymeric systems shown in Table 4, various other polymers were initially explored (including t-BOC-styrene, isobornyl acrylate and methacrylate, and t-butyl methacrylate); they were not soluble at any SC CO<sub>2</sub> test condition (up to 10,000 psi) as described in the second bimonthly report. It was quickly apparent that these modifications (i.e., adding isobornyl or t-butyl groups) to the base polymers were not sufficient to impart CO<sub>2</sub> solubility, and, thus, greater attention was focused on the fluorinated and siloxane-modified polymers.

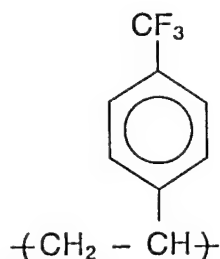
The series of coated wafers was tested for SC CO<sub>2</sub> solubility using the procedure described in section 3.2. (For clarity of presentation the processing conditions are shown together with results.) After having tested the coated unexposed wafers with SC CO<sub>2</sub>, the samples were visually examined and an estimate of the relative amount of film dissolved was made. It should be noted that this estimate was subjective; anything less than complete dissolution could be due to any of several factors including molecular weight effects, irregularities in film thickness, insoluble impurities in the film, or the CO<sub>2</sub> conditions, and certainly a more quantitative approach is intended for future studies.

One of the copolymer systems, PFM-75 (refer to Table 4), was selected for further study based on the results of the preliminary testing. Several wafers were prepared, each of which was fully exposed to a selected dose ranging from 1.4 to 20 mJ/cm<sup>2</sup> at 254 nm. These samples were then tested with SC CO<sub>2</sub> at various conditions, and the remaining film thickness was measured. Finally several wafers coated with the PFM-75 copolymer were exposed at 254nm through large feature masks and developed with SC CO<sub>2</sub>. The siloxane-modified methacrylates were further studied as well; coated wafers were exposed through a large feature mask and developed.

**Table 4. Polymers tested as negative resists with SC CO<sub>2</sub> developing**

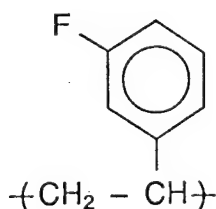
### Fluorinated Styrenes

#### 4 - TFMS



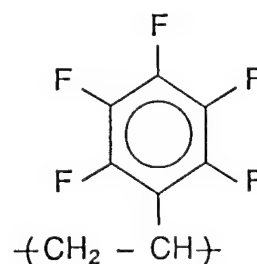
4 - Trifluoromethyl Styrene

#### 3 - FS



3 - Fluorostyrene

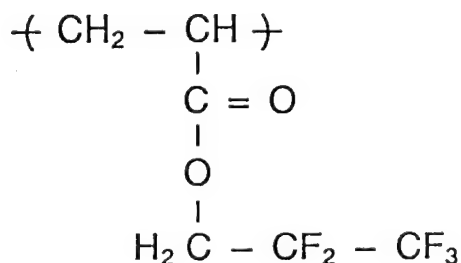
#### PFS



2,3,4,5,6 - Pentafluorostyrene

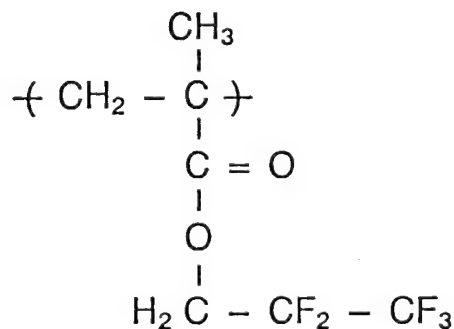
### Fluorinated Acrylates, Methacrylates

#### PFA



2,2,3,3,3 - Pentafluoropropyl Acrylate

#### PFM



2,2,3,3,3 - Pentafluoropropyl Methacrylate

Table 4. Polymers tested as negative resists with SC CO<sub>2</sub> developing (continued)

Fluoromethacrylate/t-butyl Methacrylate Copolymers

PFM	TBMA	Composition (mol ratio PFM/TBMA)
$\begin{array}{c} \text{CH}_3 \\   \\ \text{-(CH}_2\text{-C)-} \\   \\ \text{C=O} \\   \\ \text{O} \\   \\ \text{H}_2\text{C-CF}_2\text{-CF}_3 \end{array}$	$\begin{array}{c} \text{CH}_3 \\   \\ \text{-(CH}_2\text{-C)-} \\   \\ \text{C=O} \\   \\ \text{O} \\   \\ \text{C(CH}_3\text{)}_3 \end{array}$	PFM-90: 90/10 PFM-75: 75/25 PFM-50: 50/50 PFM-30: 30/70 PFM-20: 20/80 PFM-10: 10/90

Siloxane-Modified Methacrylate/t-butyl Methacrylate Copolymers

(A)	(B)	Composition (mol ratio A/B)	Architecture
$\begin{array}{c} \text{CH}_3 \\   \\ \text{-(CH}_2\text{-C)-} \\   \\ \text{C=O} \\   \\ \text{O-(CH}_2\text{)}_3\text{-Si(CH}_3\text{)}_2\text{-O-Si(CH}_3\text{)}_3 \end{array}$	$\begin{array}{c} \text{CH}_3 \\   \\ \text{-(CH}_2\text{-C)-} \\   \\ \text{C=O} \\   \\ \text{O-C(CH}_3\text{)}_3 \end{array}$	GTP-5: 50/50 FR-5: 50/50 GTP-9: 75/25	Random Block Random

Random Siloxane Copolymers: dimethylsiloxane/diphenylsiloxane

diMe - co - diP	Mol ratio (diMe/diP)	Viscosity (cSt.)	MW
$\begin{array}{c} \text{CH}_3 \\   \\ \text{-(Si-O)-} \\   \\ \text{CH}_3 \end{array} \text{ }_x \text{ } \begin{array}{c} \text{C}_6\text{H}_5 \\   \\ \text{-(Si-O)-} \\   \\ \text{C}_6\text{H}_5 \end{array} \text{ }_y$	84/16	10,000	55,000
	84/16	500	9,300
	95/5	10,000	49,000

## 4.0 DISCUSSION OF RESULTS

### 4.1 Positive resists.

Table 5 summarizes the results of the testing with the polysilane resists; the unsensitized PCHMS resists were easily developed with SC CO<sub>2</sub>, indicating that the usual sensitizers might not be required with PCHMS formulations. The results shown in the table are for the single layer sensitized PPMS resist and for the PPMS bilayer resist (that was generated in preparation for the Phase I proposal), not shown are results for unsensitized PPMS which did not develop at any CO<sub>2</sub> condition. It is not expected, however, that the PPMS resist would develop because, generally, as the phenyl content of siloxanes is increased the solubility in SC CO<sub>2</sub> decreases dramatically<sup>1</sup>. However, it appears as though sensitization resulted in sufficient solubility of the siloxane exposure product as was evident from the single layer sensitized PPMS system. The developed single layer PPMS system is shown in the SEM in Figure 5; reasonably good 1.4 $\mu$  features are observed.

Table 5. Test Conditions and Results for Polysilanes

Sample	Exposure Wavelength	Exposure Dose (mJ/cm <sup>2</sup> )	Developing Conditions	
			3200 psi; 50°C	5600 psi; 80°C
PCHSi $\rightarrow$ PCHSiO				
• bilayer	248 nm	2 to 80	developed	developed
PMPSi $\rightarrow$ PMPSiO				
• single layer	254 nm	~ 40	-	developed
• bilayer	193 nm	~ 40	developed	developed

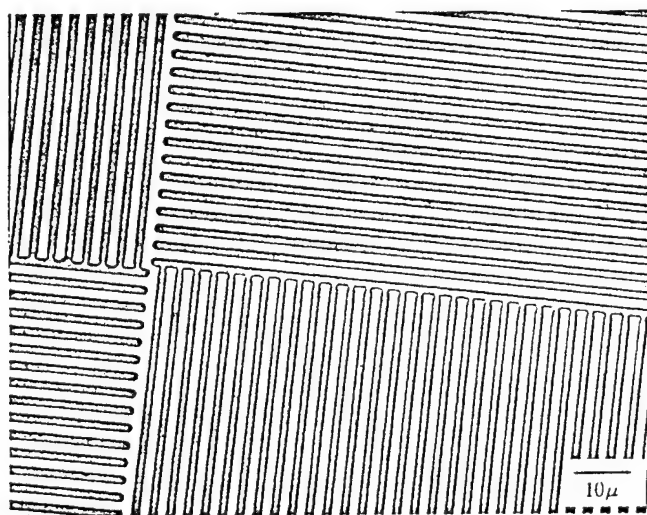


Figure 5. SEM of Single Layer PPMS Resist Developed with SC CO<sub>2</sub>

## 4.2 Negative resists

The experimental matrix of SC CO<sub>2</sub> conditions is summarized in Figure 6; the various test ranges are referred to as high, moderate, and mild to simplify subsequent presentation of the results. It is pointed out that previous experience with polymers and SCFs has indicated that not every combination of temperature and pressure is advantageous, for example, operation at high pressure and low temperature or low pressure and high temperature will not be satisfactory conditions. Each test series begins with the highest conditions; if the film was completely dissolved, another wafer with the same coating was then tested at moderate conditions, and so on. In some cases, for example with the siloxane-containing polymers and copolymers, higher temperature levels were tested at 6500 psi. A reasonable amount of CO<sub>2</sub> was passed through the chamber for each test ensuring that all the material that could be dissolved at those conditions would be dissolved. Furthermore, "successful" tests were often repeated using less CO<sub>2</sub> volume; it will be important for production to determine the minimum amount of required CO<sub>2</sub> to dissolve the unexposed film so as to minimize cycle time and increase productivity.

T (°C)	Pressure (psi)		
	6500	4000	2800
60			Mild
80		Moderate	
100	High		
120			

Figure 6. Matrix of Test Conditions for Negative Resists

The following series of figures summarizes the results of testing the unexposed coated wafers under the various SC CO<sub>2</sub> conditions; the degree of removal (i.e., dissolution) reported is, again, a subjective qualitative analysis based on visual inspection of the wafers after testing, and may actually reflect the film quality (impurities, imperfections, etc.) rather than solubility. Future work will involve more quantitative analyses of remaining film.

**4.2.1 Fluorinated styrenes.** Figure 7 summarizes the test results obtained with the fluorinated styrene compounds. These polymers would be most useful with DUV (248nm) exposure tools in single layer applications. While the 3-fluorostyrene was relatively insoluble even at the most severe conditions, it appears as though the higher degree of fluorination of the other two polymers was sufficient to dramatically enhance their solubility even at mild conditions.

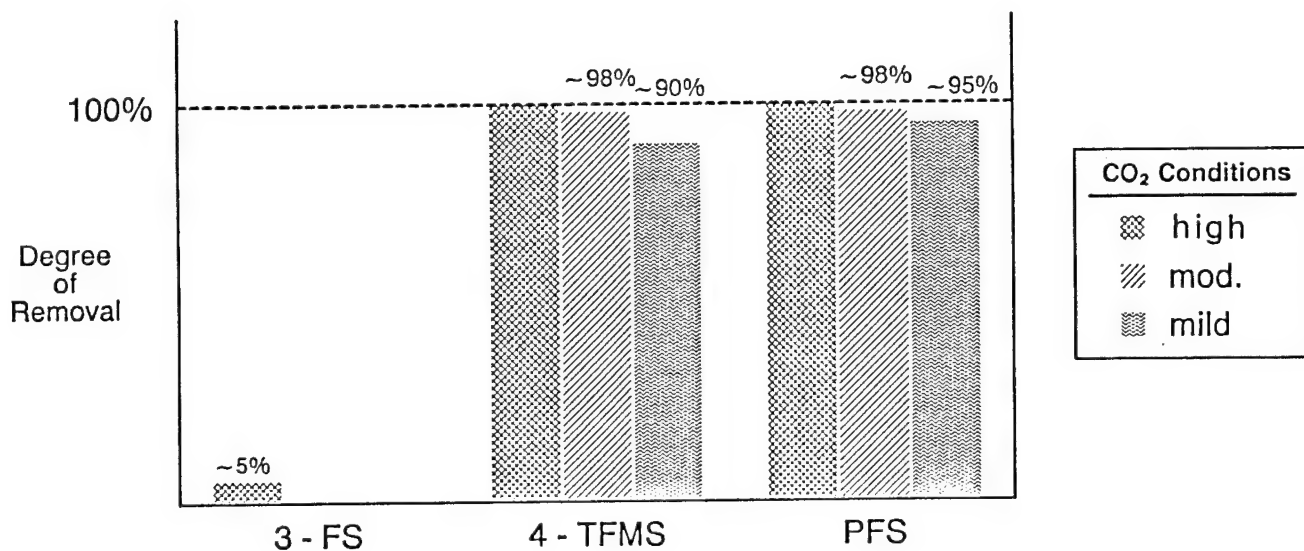


Figure 7. Test Results for Fluorinated Styrenes

**4.2.2. Siloxane copolymers.** Tests results with random dimethyl/diphenyl (diMe/diP) siloxane copolymers are summarized in Figure 8. The polymers were obtained from Gelest, Inc. (Tullytown, PA) and represent two different compositions and viscosities (as specified in Table 4). These polymers are of interest for bilayer applications because the silicon provides an etch barrier. At high CO<sub>2</sub> conditions the lower phenyl-content copolymer was the most soluble, and at a higher temperature the lower molecular weight (and viscosity) copolymer was the most soluble. It is obvious that depending upon operating conditions either molecular weight or composition (or both) will have a dominating influence on solubility in SC CO<sub>2</sub>.

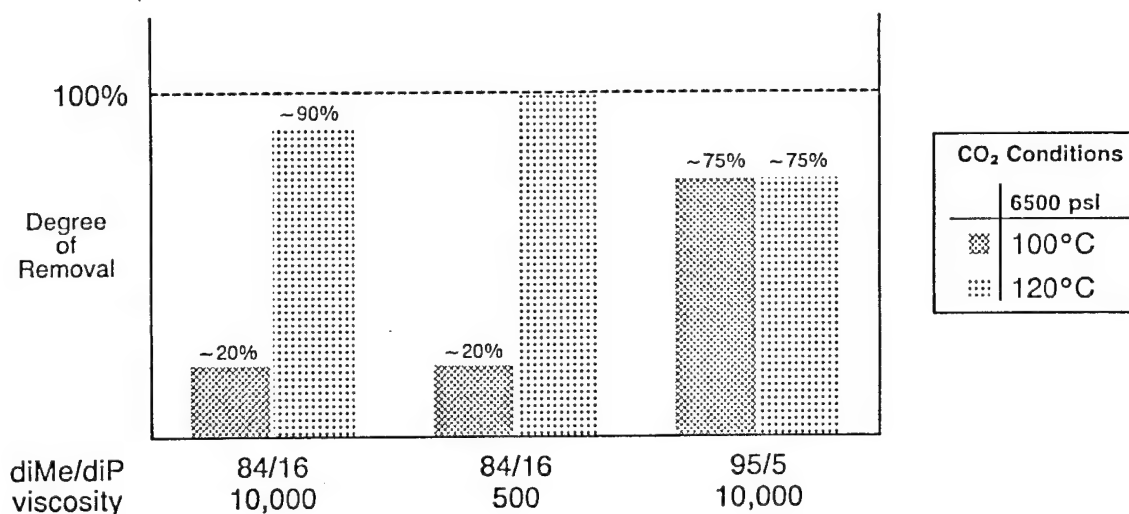


Figure 8. Test Results for Siloxane Copolymers

**4.2.3 Siloxane-modified methacrylates.** This unique category of polymers offer an advantageous combination of properties. Methacrylates are used with 193nm lithography but are not very etch resistant unless certain compounds are added to the formulation. Therefore their use is primarily limited to single layer systems. However, incorporation of the siloxane groups provide an inherent etch barrier now increasing the range of application to bilayer systems as well.

It is clear from the results presented in Figure 9 that the higher siloxane-containing copolymer was readily soluble in SC CO<sub>2</sub>, even at moderate conditions, and that decreasing the siloxane content has a dramatic negative influence on solubility. The effects of architecture (i.e., random vs block) is unknown based on this test series and would have to be explored at different compositions. (Note: in the figure, SiOMA/TBMA refers to the mole ratio of the siloxane-containing methacrylate to t-butyl methacrylate which are copolymerized.)

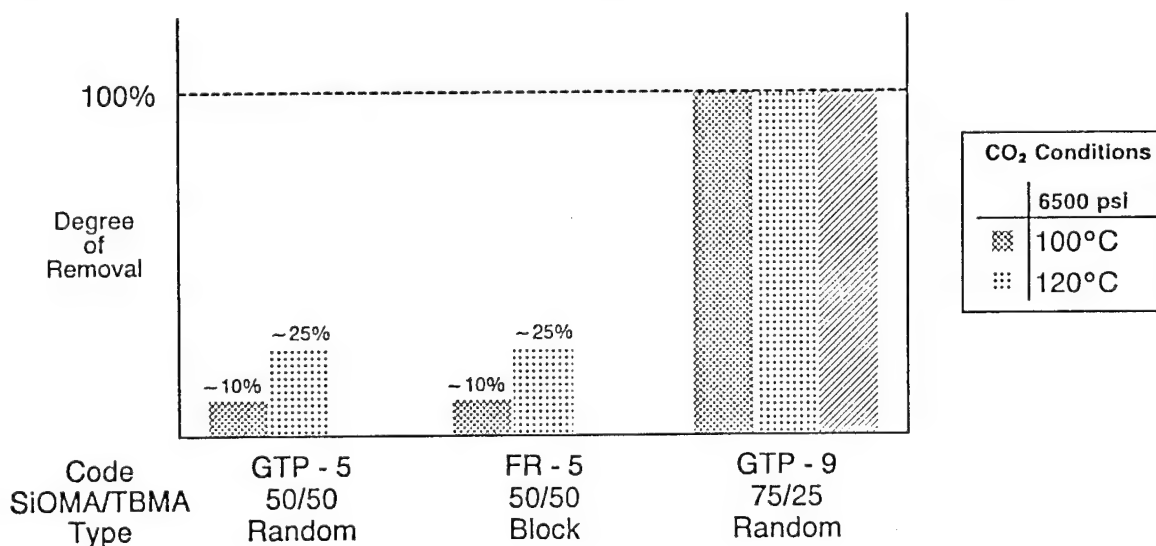


Figure 9. Test Results for Siloxane-Modified Methacrylates

**4.2.4. Fluorinated Acrylics.** Two categories of fluorinated acrylics were investigated: pentafluoropropyl acrylate (PFA) and -methacrylate (PFM) homopolymers, and copolymers of PFM and t-butyl methacrylate (refer to Table 4 for composition). The homopolymers were very soluble at all test conditions, as shown in Figure 10. For this reason a range of copolymer compositions was studied to target the minimum amount of fluorinated polymer required to give suitable solubility in SC CO<sub>2</sub>, and still maintain suitable imaging characteristics. The copolymers containing higher amounts of fluorinated polymer were soluble at high and moderate conditions, but not completely soluble at the mild conditions, Figure 11. This result is most likely due to molecular weight effects because impurities in the film would have been observed as residue at the higher conditions. At compositions of 50/50 (PFM-50) and lower, moderate conditions were not sufficient for completely dissolving the film. Higher CO<sub>2</sub> conditions (6500 psi, 100°C) successfully dissolved those copolymers having 30 mole% and higher PFM content.

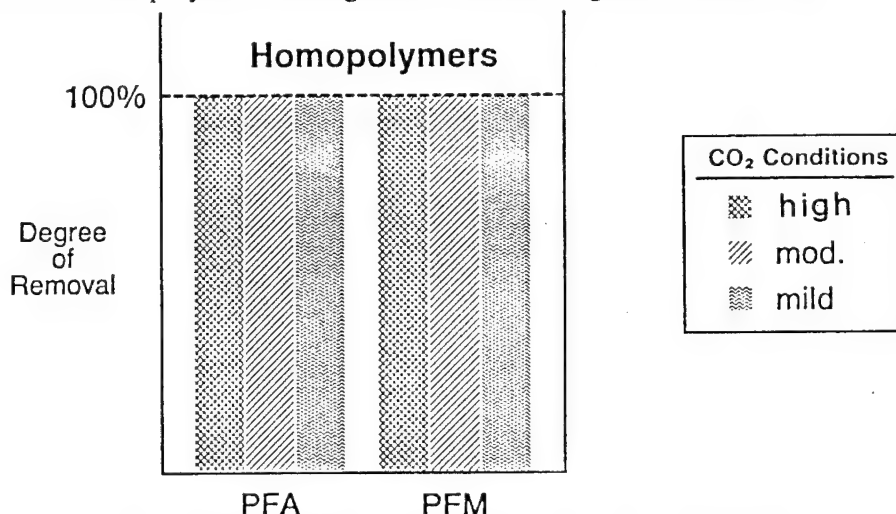


Figure 10. Test Results For Fluorinated Acrylics-Homopolymers

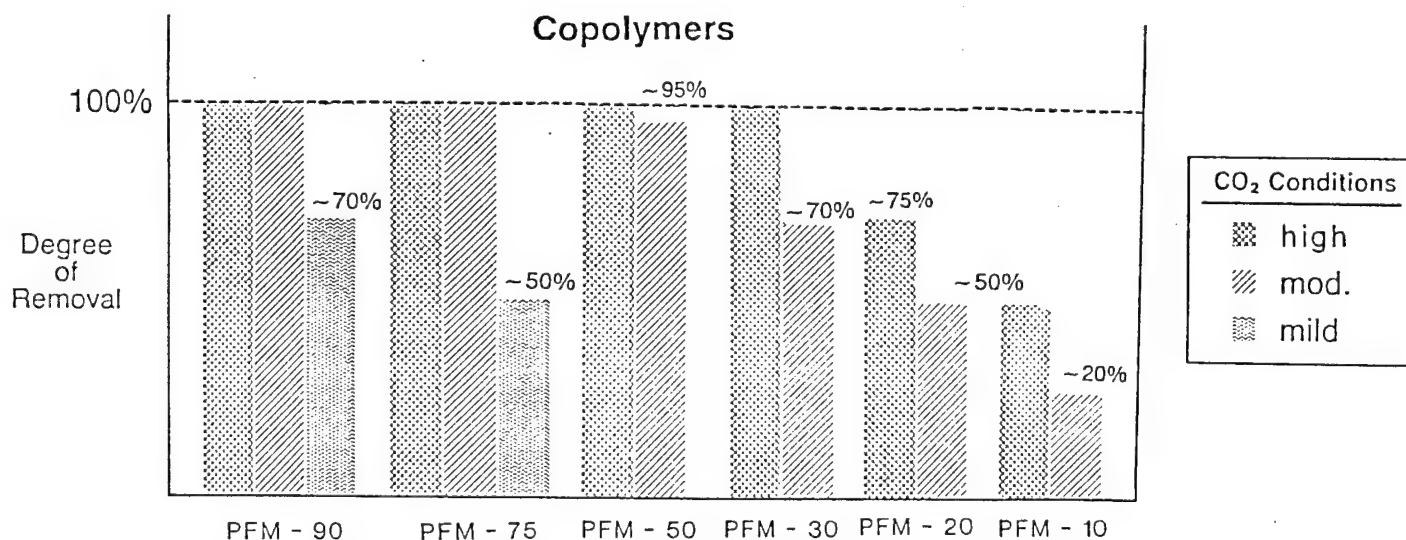


Figure 11. Test Results For Fluoromethacrylate Copolymers



### 4.3 Exposure/Solubility Relationship

Based on the excellent solubility results in the previous section, PFM-75 was selected for exposure testing. Several test wafers were prepared with PFM-75 formulated with a standard onium salt photoacid generator, and fully exposed at 254nm to doses ranging from 1.4 to 20 mJ/cm<sup>2</sup>. After exposure the samples were baked to remove t-butyl ester groups thereby generating multi carboxylic acid groups in the polymer; such a polymer is insoluble in SC CO<sub>2</sub> and therefore satisfies the requirement for producing a negative image. The wafers were then tested with SC CO<sub>2</sub> using conditions presented in Figure 6. The objective was to ultimately determine the exposure dose and developing conditions required for complete insolubilization. Measurement of the remaining film thickness indicated that at exposure doses less than 8.5 mJ/cm<sup>2</sup> essentially the entire film was dissolved even at mild SC CO<sub>2</sub> conditions. At 20 mJ/cm<sup>2</sup>, there was no detectable dissolution of the film in SC CO<sub>2</sub> using mild and moderate conditions. Thus, an appropriate minimum exposure dose would fall within the range of 8.5-20 mJ/cm<sup>2</sup> for good imaging. Figure 12 summarizes the results of the exposure/solubility tests; the curves are plotted in a similar fashion to contrast curves generated by developing in a liquid solvent, e.g., remaining film thickness after developing versus log of exposure dose. (The data is equivalently plotted on semi-log graph paper as shown.) Examples of typical contrast curves for liquid developing is shown for comparison in Figure 13. Although in Figure 12 there is not yet enough data to fill in a continuous curve, it appears as if a similar trend is emerging.

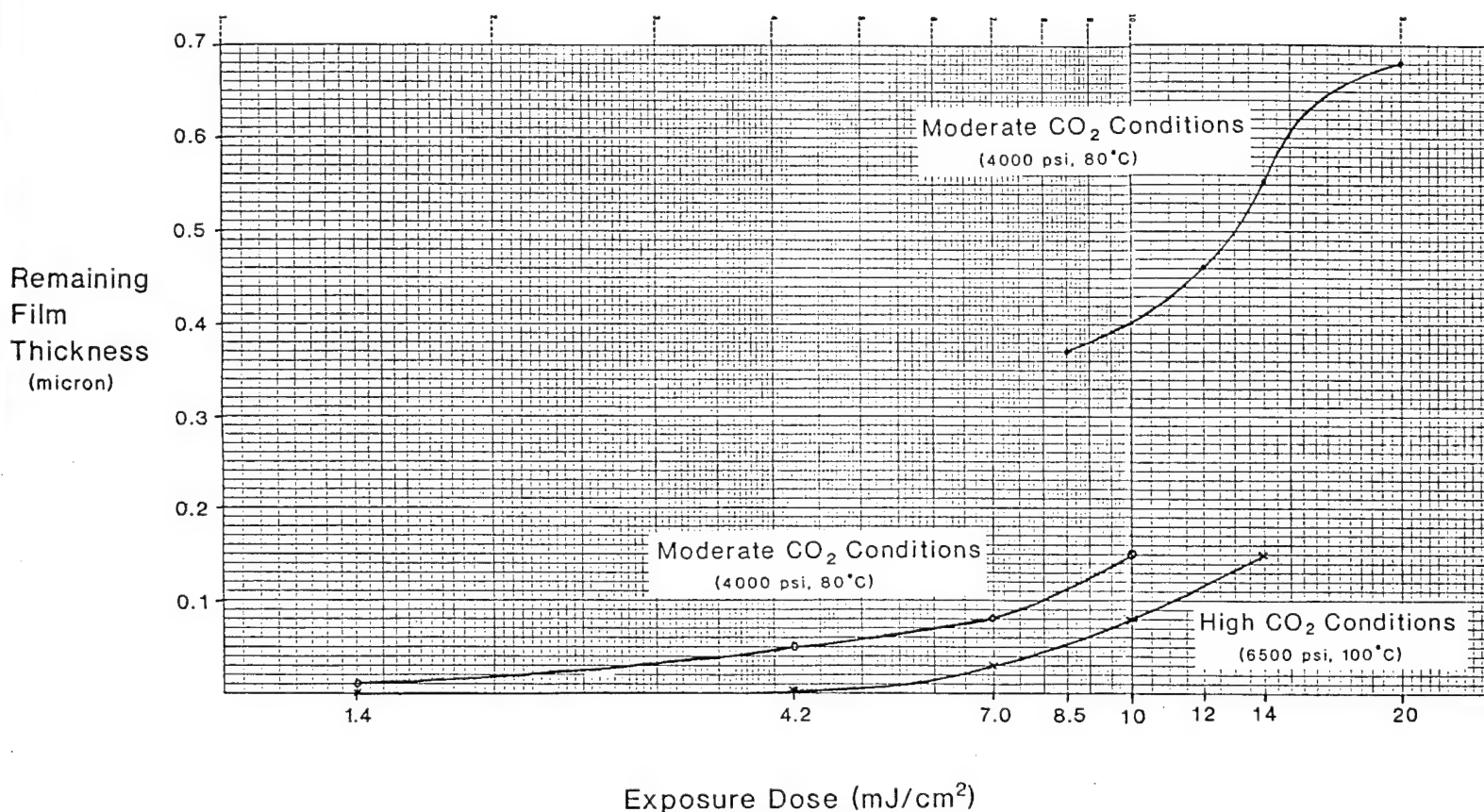
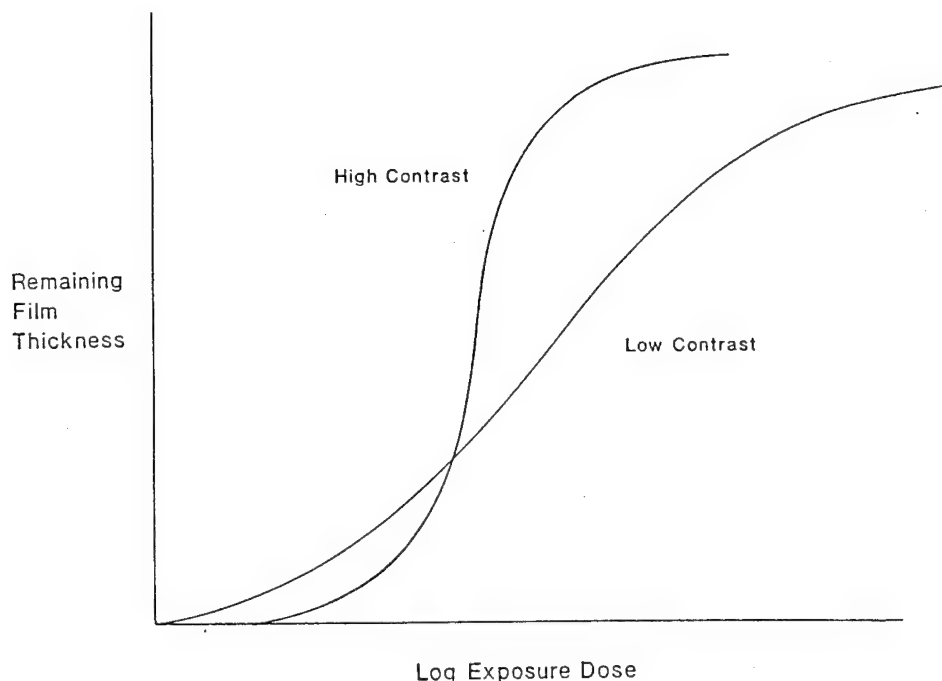


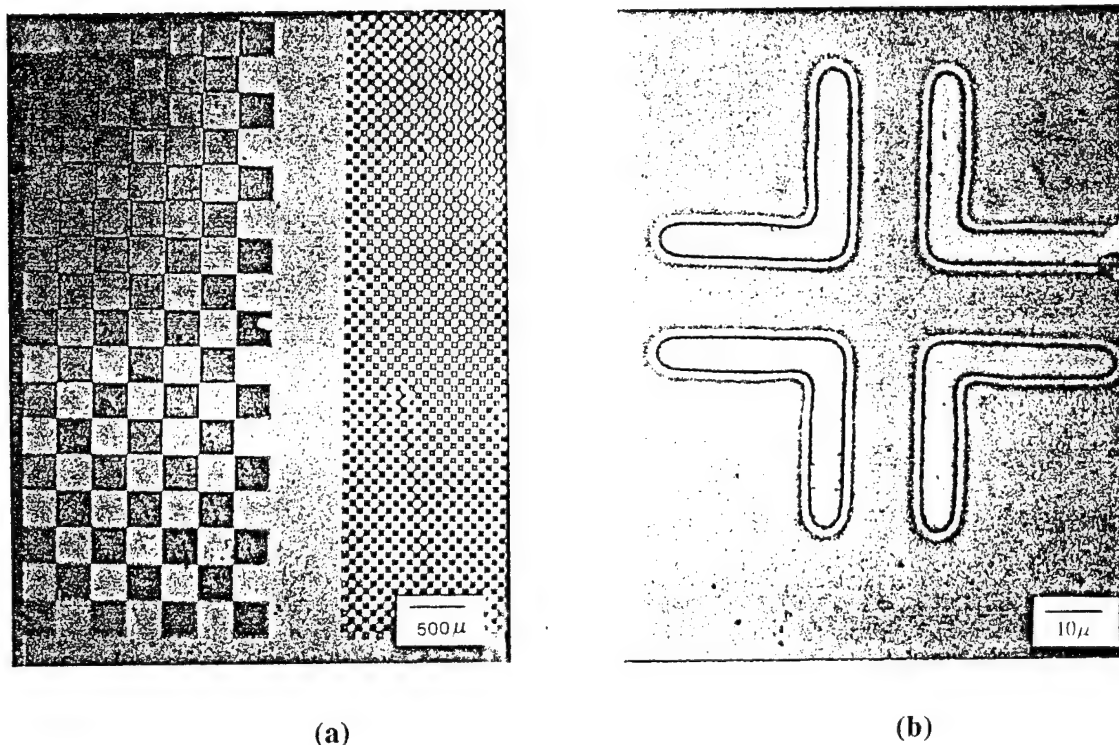
Figure 12. Exposure/Solubility Relationship for PFM-75



**Figure 13. Typical Shapes of Contrast Curves Generated for Liquid Developers**

#### **4.4 Imaging**

In order to demonstrate imaging capabilities, several wafers were prepared with PFM-75 or GTP-9, a siloxane-modified methacrylate. (Refer to Table 4 for composition.) For the PFM samples, the wafers were spin-coated, baked at temperatures above 100°C for 1 minute, exposed at 254nm, then baked again at above 100°C for 1 minute. Two exposure doses, 15 mJ/cm<sup>2</sup> and 20 mJ/cm<sup>2</sup>, were tested. As a simple first demonstration of developing capabilities, the wafers were partially masked with a razor blade (a common practice for providing information about the ability of a developer to selectively dissolve only one portion of the resist). Both wafers were successfully developed at moderate conditions (4000psi, 80°C); it was easy to observe the dramatic results- one half of the film (the unexposed portion) had been completely dissolved down to the substrate, and the other half was untouched. Exposure was then conducted using large feature masks having "checkerboard" patterns with mask openings of 10 to 100μ. The samples were developed using test conditions which previously indicated no detectable dissolution of the film from the fully exposed wafers yet complete solubility of the unexposed film, i.e., 4000psi, 80°C. Figure 10 (a and b) are optical micrographs of a wafer exposed at 20 mJ/cm<sup>2</sup> and developed with SC CO<sub>2</sub>. The unexposed film was indeed selectively dissolved down to the substrate. Figure 10b shows an image from one of the pads; it too is developed to the substrate. The distortions along the edges of the image are suspected to be due to over baking at a temperature greater than T<sub>g</sub>.



**Figure 14. Optical Micrographs of SC CO<sub>2</sub> Developed Images  
(PFM-75 film; 20 mJ/cm<sup>2</sup> at 254nm)**

The CO<sub>2</sub> soluble siloxane-modified GTP-9 was also used to carry out preliminary imaging studies. The coated wafers were exposed through a mask with a 1.0 cm<sup>2</sup> opening in the center at 248nm with exposure doses of 20 mJ/cm<sup>2</sup> and 80 mJ/cm<sup>2</sup>. Each sample was first tested at moderate CO<sub>2</sub> conditions, but the unexposed portions did not completely dissolve. This was at first surprising because those SC CO<sub>2</sub> conditions previously had successfully dissolved the unexposed films of GTP-9 (see Figure 9). It was later suspected that the routine post-exposure bake may have been carried out at too high of a temperature. At conditions of 6500psi and 100°C each of the samples was successfully developed.

## **5.0 OTHER CONSIDERATIONS-SC CO<sub>2</sub> "Dry" Developing vs Wet Developing**

Besides demonstrating technical feasibility of the SC CO<sub>2</sub> developing process, it was important for this program to evaluate the impact on waste, efficiency, and cost if this process were to be implemented in manufacturing operations. This section discusses these other important considerations.

Two of the program's objectives were to compare the SC CO<sub>2</sub> developing process with conventional wet processes, particularly to demonstrate waste reduction and product improvement. It is relatively easier to address the waste issues than it is to address quantitative improvements in product quality, primarily because the resist systems studied represent next-generation materials that are not currently in use. Furthermore, the limited amount of imaging performed on this program does not provide an adequate baseline for comparison with wet processes. However, an assessment of the anticipated improvements in product quality can be made.

### **5.1 Waste**

A significant fraction of the chemical waste stream from conventional lithographic processes arises from the developers used to produce lithographic patterns. The predominant photoresist developers used today are aqueous base solutions such as tetramethylammonium hydroxide (TMAH) in water, although for some photoresists, especially bilayer systems which contain siloxanes and are insoluble in aqueous solutions, organic solvents such as isopropyl alcohol are still in use. These solutions are utilized in large volume because wafers are developed in a "single wafer" mode and each solution is used only once. In addition, an equal amount of water rinse is required after developing, and the wafer must then be dried.

As an example of the magnitude of waste generation solely from the lithographic process, each wafer has at least 15 levels of lithography which collectively utilize about 750 ml of developer solution and 750 ml of water rinse. Thus, for a large semiconductor line which produces 5,000 finished wafers per day, the total volume of contaminated water (developing solution plus rinse) is 2000 gal/day or 600,000 gal/yr.

Implementation of the SC CO<sub>2</sub> developing process can eliminate all of this generated waste. The gas is recirculated in full-scale processes, and because of the continuous flow nature of the SC CO<sub>2</sub> process multiple wafers can be developed in a single batch rather than individually. Although the minimum CO<sub>2</sub> requirements have not yet been determined, it is projected that literally less than five lbs of CO<sub>2</sub> could develop 60-80 wafers per batch, or ~20-30 grams of CO<sub>2</sub> per wafer. Waste disposal is greatly simplified in the SC CO<sub>2</sub> process because during the pressure-reduction stage in the process (refer to Figure 4 and corresponding description), the dissolved resist precipitates as a solid and is collected in concentrated form. Because of the small amount of resist on each wafer there is very little solid waste; it is projected that only a few hundred grams per month of polymer powder would be generated.

Finally, it is necessary to address the concern about perceived contribution to global warming of SC CO<sub>2</sub> processes. Most importantly, CO<sub>2</sub> used for all current industrial extraction processes is derived from natural sources, such as fermentation, and thus it remains within an "ecological envelope"; no additional CO<sub>2</sub> is added to the atmosphere. Furthermore, and almost

irrelevant in light of its source described above, the amount of CO<sub>2</sub> actually released to the atmosphere, even in very large scale operations, is relatively negligible in comparison with automobile emissions, for example. Therefore, there is no global warming consequence of using SC CO<sub>2</sub> processes.

## **5.2 Safety and Handling**

SC CO<sub>2</sub> is a particularly advantageous alternative to liquid developers because of its environmental attributes: it is non-ozone depleting, non-toxic, non-flammable, and "worker friendly". Since the gas is fully contained within a recirculating system (and certainly because it is a gas and not a liquid), it is never physically "handled".

One of the most serious safety problems with liquid developing are the fumes that are generated during developing. At every developing station there must be a laminar flow hood, a rather expensive piece of equipment. With the particular polymers investigated on this program, especially those which are normally considered positive resists, those fumes will not be generated during SC CO<sub>2</sub> developing because only the unexposed portions (to create negative images) are dissolved rather than the exposed portions, and a different exposure and dissolution chemistry is involved. Furthermore, if there are any fumes generated during SC CO<sub>2</sub> developing they will be contained within the recirculation loop and are readily stripped from the CO<sub>2</sub> by passing the stream through activated carbon (a routine processing practice). For silicon-containing polymers, flammable solvents such as isopropyl alcohol pose a safety risk during the developing step; CO<sub>2</sub> can eliminate this risk and has been demonstrated as a developer for these polymers.

As mentioned in the previous section, the only "waste" associated with the SC CO<sub>2</sub> process is a projected few hundred grams per month of polymer powder. Therefore, the waste handling and disposal problems are reduced by literally orders of magnitude especially since solids are more easily disposed of than are liquids. There are absolutely no solvent disposal problems.

Some have suggested that high pressure equipment can be unsafe, but this comment usually comes from personnel unfamiliar with supercritical fluid processes. All high pressure processing systems are equipped with standard safety features such as pressure relief valves, rupture discs, and other controls in the unlikely event of a pressure excursion. High pressure operation is quite common in the chemical process industry; high pressure polymerization of polyethylene, for example, is carried out at 40,000 psi (!) on a large scale. The SC CO<sub>2</sub> coffee decaffeination process (General Foods, Houston TX) operates at 5000 psi with extraction vessels 70 ft high x 7 ft dia. processing coffee at 50,000,000 lbs/yr. Manufacturers of high pressure equipment for CO<sub>2</sub> processing are highly qualified and conscientious about safety features and controls.

## **5.3 Product Performance**

There are essentially two ways of comparing the influence of the developing process on image quality; one is to compare contrast curves (which predict image contrast and resolution) generated by each method and the other is to compare the actual images. Neither method can currently be used, however, in the case of SC CO<sub>2</sub> developing because there is as yet no

adequate baseline for comparison. Resist systems that by conventional wet developing produce positive images have been used on this program to produce negative images via SC CO<sub>2</sub>. Therefore, it is an "apple-orange" situation to try and compare negative and positive images except in the most general terms, and certainly only after carrying out significant imaging studies with SC CO<sub>2</sub> developers. Even if a non-polar liquid solvent was used to reproduce a negative image, at the feature sizes thus far investigated the differences would be too subtle to detect. Furthermore, this would not be a comparison of SC CO<sub>2</sub> developing with any traditional wet developing method, but essentially a comparison of two "new" methods.

It is expected that as feature size and circuit geometry is reduced, several problems which are not so severe at the 0.5 $\mu$  image level will prove to be very serious at the sub-half micron levels. Those problems include swelling of the resists and a phenomenon known as resist pattern collapse<sup>4</sup>. Swelling problems are quite common with all liquid developers, and for this reason the developer contact time must be strictly controlled. During conventional liquid developing there is an end point beyond which the developer begins to attack the insoluble portions (i.e., the images) of the resist leading to swelling and loss of resolution. This is especially troublesome with bilayer systems because of the extremely thin (<0.1 $\mu$ ) photoresist layer. If there is any distortion of the resist layer, the subsequent etching step will not produce high quality images; the substrate, then, cannot be processed with the required precision. In all of the SC CO<sub>2</sub> developing studies, including the one originally described in the Phase I proposal, the developing was carried out well beyond the end point without noticeable damage to the remainder of the film. Although the actual SC CO<sub>2</sub> end point has not yet been determined, it is predicted that with such thin films very little gas per wafer (on the order of 10s of grams) will be required; experiments carried out on this program used several hundred grams of CO<sub>2</sub> per wafer. However, the finding that SC CO<sub>2</sub> developing can be carried out beyond the endpoint increases the flexibility and versatility of this process. The developing costs associated with liquids and stringent quality control and product loss or rejects due to bypassing the end point will be minimized or completely eliminated with SC CO<sub>2</sub>.

Resist pattern collapse is an especially severe problem with sub-half micron images. This phenomenon is a physical collapse of resist images due to the surface tension of liquid developers. As a wafer is removed from contact with the developer solution the surface tension forces, now being unequally distributed as the liquid evaporates, are strong enough to literally knock over the images. Gases (and supercritical fluids), however, have no surface tension effects. Even at the end of the SC CO<sub>2</sub> developing cycle when the chamber is emptied of gas, the fluid never passes through the liquid phase. Therefore, the threat of resist pattern collapse would never be encountered in SC CO<sub>2</sub> developing.

While a side-by-side comparison of the efficiency of SC CO<sub>2</sub> vs liquid developing in producing quality images is difficult at this early stage, it is possible to suggest product improvements and process versatility that can be expected with the combined use of the new resist systems (and even the conventional resists) and SC CO<sub>2</sub> developing:

1. The solubility properties are adjustable (by changing pressure and/or temperature); therefore, a number of different resist polymers can be developed using the same piece of equipment with simple pressure and temperature adjustments.



2. The SC CO<sub>2</sub> developing process is more flexible than liquid processes because of the adjustable solvent properties and especially the minimal concern of developing beyond the end point. This will reduce product loss due to bypassing the endpoint which can occur with liquids, and will minimize quality control costs.
3. The physical properties of SC CO<sub>2</sub> (liquid-like density, gas-like viscosity and diffusivity, and zero surface tension) allow the fluid to penetrate extremely small dimensions ( $<0.1\mu$ ), a requirement for next-generation developers which will limit the use of most liquid developers because of their surface tension. Thus, swelling problems and resist pattern collapse can be eliminated.
4. The ability to produce both positive and negative images (depending on the resist system) and to apply the process with bilayer and single layer systems extends the use and versatility of SC CO<sub>2</sub> developing.
5. It is expected that SC CO<sub>2</sub> developing can be used to process many, many wafers at a time versus the "single wafer" mode for liquid developers. Productivity, therefore, can be greatly increased.
6. Because negative images have been shown to be more efficient than positive images for information processing, the use of SC CO<sub>2</sub> to develop negative images using traditional positive resists will inherently improve product performance.
7. The properties (molecular weight, composition, functionality, etc.) of the modified polymers designed specifically for developing by SC CO<sub>2</sub> can be tailored for a variety of lithographic applications. The use of these polymers would be limited or even impossible with traditional liquid developers.
8. Features such as etch resistance, 193nm absorbance and optical transparency, sensitivity, and SC CO<sub>2</sub> solubility, can be designed into the resist to minimize or eliminate the use of common additives which add to the cost of the resist.

There is certainly a great deal of further research required to show conclusively that the product quality of semiconductors is improved by SC CO<sub>2</sub> developing of images. However, the process benefits described above indicate that there are advantages in using SC CO<sub>2</sub> developing, especially as feature size becomes increasingly smaller and as environmental regulations become increasingly more stringent. Other issues that have not yet been addressed are equipment and costs. The next section gives a preliminary evaluation of these important manufacturing factors.

## **6.0 PRELIMINARY EQUIPMENT DESIGN AND ECONOMIC ASSESSMENT OF SC CO<sub>2</sub> DEVELOPING**

Throughout the Phase I program serious consideration has been given to future equipment requirements. At each integrated circuit manufacturing facility there are several solvent developing stations, each station equipped with spinners, developing chambers, a laminar flow hood for solvent abatement, and drying ovens. The "footprint" i.e., the area the equipment covers, then, is quite large, estimated at 8' x 20', and each must be in a class 1000 clean room. One important requirement for the SC CO<sub>2</sub> developing equipment must be a relatively small

footprint. Other requirements include ease of operation, proper safety features, and clean room compatibility.

The equipment design requirements need to be based on current manufacturing levels; this in turn provides a basis for an economic assessment. It was mentioned previously that a large semiconductor manufacturing facility produces 5000 finished wafers (8" dia) per day; this is selected as the basis for the equipment design and economic evaluation.

The average capacity of a lithographic exposure tool (called a stepper) is 50-60 wafers/hr; a simple calculation indicates that a large facility would have a minimum of four steppers processing wafers around the clock, or several steppers operating one or two shifts. Since each stepper is a multi-million dollar piece of equipment it is assumed that 24 hr operation is carried out with the four steppers. The SC CO<sub>2</sub> developing equipment would have to accommodate this production volume which will certainly not present a problem. There are many additional unknown operational factors that have to be considered including the following:

1. Will the developing step be on-line or off-line?
2. If off-line, how many shifts/day will the operation be carried out?
3. If on-line, what are the requirements for cycle time?
4. Is there any accumulation of inventory to be developed?

In order to generate an equipment design many assumptions will have to be made at this stage regarding integrated circuit manufacturing. It is assumed, for example, that the developing step is carried out off-line; that is, multiple wafers are exposed in a given time period then the entire batch is developed. It is also assumed that each stepper will have its own developing station so that the processing requirement for an individual developing station is 60 wafers/hour. This is a quite reasonable cycle time for SC CO<sub>2</sub> developing which includes loading the wafer tray into the chamber, sealing the system, filling with CO<sub>2</sub> and achieving the desired temperature and pressure, carrying out the developing, depressurizing, and unloading the vessel. Since the coated wafers are approximately 2mm thick, and assuming a maximum spacing between wafers of ~5mm, a tray containing 60 wafers will only require a vessel length of ~50cm or ~20". This is actually a rather small processing chamber relative to most SCF equipment. The inside diameter of the chamber will need to be only slightly bigger than 20cm to accommodate the 8" wafers and tray.

There are several ways of designing efficiency into SCF equipment. For example, two chambers are often used to maintain processing continuity; as one vessel is being operated, the other can be unloaded and reloaded in preparation for operation. Vessels can be designed with "quick-opening" breech closures versus bolt closures if timing is critical. Complete automation and process controls can be integrated to minimize manual interaction. These are just a few of the features that are available, and each can have a beneficial impact on the economics.

In critical manufacturing operations such as semiconductor processing, most of the work is carried out in a clean room environment. The SC CO<sub>2</sub> developing system can be operated in a clean room with the auxiliary equipment (such as the compressor) located in an adjacent non-



clean room. This configuration was employed for an SCF cleaning system that Phasex installed at Newark Air Force Base (in November 1993). Since clean room space is very limited, it makes the most sense to set up the auxiliary equipment in separate areas, with the developing chamber, separator, controls, and appropriate piping in a fully enclosed system located inside the clean room. The footprint for the clean room equipment would be relatively very small, estimated at 4'x 6' for the dual-vessel configuration.

The equipment design for SC CO<sub>2</sub> developing is based on the following (some of the features such as pressure rating and compressor capacity are overcompensating since optimization has not yet been carried out):

Batch Size: 60 wafers (spaced ~5mm apart in stainless tray)  
Cycle duration: 1 hour (includes loading, operating, and unloading)

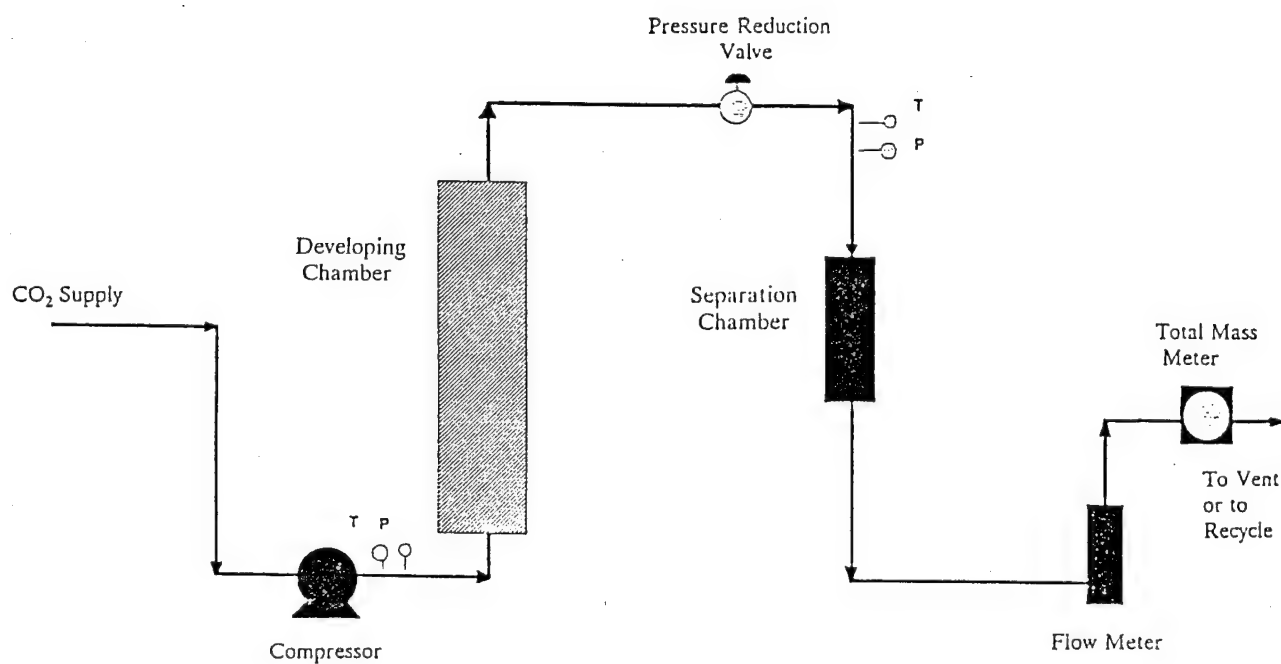
Primary developing chamber requirements:

- 8.5-9" ID x 20" L
- Rated up to 6500 psi pressure; 150°C (probably much higher than required)
- "Quick-opening" closures

General system requirements:

- Separator vessel: stainless steel; rated for 2500 psi, 100°C
- Compressor: up to 12 lb/hr liquid CO<sub>2</sub> delivery (a non-contaminating diaphragm compressor is recommended)
- All piping and valves: stainless steel, rated for 10,000 psi
- Standard safety features: rupture disc, pressure relief, etc.
- Digital controls and instrumentation
- Fully enclosed unit; compressor and CO<sub>2</sub> cylinder storage located outside clean room
- Footprint ~4' x 6' (allows for two developing chambers)
- Options include:
  - additional developing chamber(s) for smaller, 4" or 1" wafers
  - computer control operation
  - in-line monitoring

The majority of the equipment components are standard items; the developing chamber and the internals (tray) may require custom fabrication. The cost for a single chamber system, based on prior experience with high pressure equipment, will range from \$150K-200K including design and installation. The optional features could add as much as \$200K to the cost depending on the magnitude of the required controls and monitoring. This is a realistic preliminary estimate and is a quite small figure in comparison with typical lithographic equipment. A preliminary schematic diagram for the system is shown in Figure 15.



**Figure 15. Schematic Diagram of Preliminary Prototype SC CO<sub>2</sub> Developing System**

## **7.0 PRELIMINARY COMMERCIALIZATION PLAN**

The early steps have already been taken toward the eventual goal of commercialization; that is, involvement of potential users. The preliminary results of this program were presented at the '95 International Symposium on Microlithography held in Santa Clara, CA (Feb. 19-24, 1995), and they generated considerable interest among the attendees. The audience was nearly 200 strong, composed of industry, government, and academia involved in lithography from around the world. PhaseX has since received numerous requests for copies of the manuscript that was presented.

The decision to involve IBM as a subcontractor on this program was a strategic one. The company is internationally recognized as a leader in photoresist technology and possesses the expertise in lithography to guide this effort toward the objective of commercialization. Through their joint research agreement with MIT Lincoln Laboratory (Lexington, MA) to develop 193nm technology, they have associations with some of the most widely respected researchers in lithography and have access to the latest state-of-the-art equipment. The SC CO<sub>2</sub> developing process complements their ongoing effort and is being viewed with enthusiasm.

IBM's knowledge, generally, of integrated circuit manufacture, and, specifically, lithographic operations, have provided the realistic approach that this program required. They have related, for example, that in order to maintain competitiveness in the global market, there must be full-scale commercial production of semiconductors using 193nm lithography for 0.18 $\mu$  generation by the year 2000. Within the next three years the prototype equipment for this technology will be developed. The opportunity for incorporating new photoresist developing techniques such as SC CO<sub>2</sub> into manufacturing is very strong at this stage of development, but the opportunity will be lost once 193nm technology is in place commercially. At the very least, the SC CO<sub>2</sub> developing technology will be much more difficult to integrate into manufacturing at a later time.

Since the requirements for advanced semiconductor technology is constantly changing it is crucial to anticipate the future needs of the electronics industry. Processes and equipment that are versatile enough to accommodate the growth and advancement of the technology must be implemented. Integration of SC CO<sub>2</sub> technology at this early stage is expected to provide the necessary process flexibility to find long term use as an environmentally responsible and efficient photoresist developer and not just a transitional solution.

Since the electronics manufacturers are already anticipating significant changes in their current processing operations in order to meet near-term and future needs, the initial approach to commercialization of SC CO<sub>2</sub> developing is to demonstrate that the process will be effective with next-generation resist systems as well as with current systems. It has been demonstrated on this program that SC CO<sub>2</sub> developing is feasible with polysilanes, polysiloxanes, fluorostyrenes, and modified methacrylate copolymers, which represent polymer systems currently used in resists as well as those being investigated for next-generation resists. The best way to inform potential users of the utility of SC CO<sub>2</sub> developing is by continuing to publicize the results of this effort and to continue to show increasing proof of performance improvements and advantages over liquid developers. This is the next step in the commercialization plan, and it can only be achieved through further research. Subsequently, it is planned to build a prototype demonstration unit, and hopefully with the cooperation of IBM, to demonstrate to the

electronics industry the ease with which the SC CO<sub>2</sub> developing process can be implemented in manufacturing operations. It is further intended to advertize this new developing process as an environmentally responsible alternative to traditional liquid developing for currently used resists, and for use with some of the next-generation resists as a combined package.

The association with IBM on this program has lent significant credibility to the preliminary findings in the eyes of the electronics industry; people do take notice of a leader such as IBM. However, even an electronics giant would not yet invest in what is considered high risk technology without further investigation. It is hoped that a Phase II effort will follow, allowing the benefits of SC CO<sub>2</sub> developing to be more quantitatively demonstrated, i.e., a next-generation developer for next-generation resists.

## **8.0 CONCLUDING REMARKS**

The results of this Phase I program demonstrate that SC CO<sub>2</sub> developing of photoresists is a viable technique for many conventional resist systems (polysilanes and polysiloxanes) and for many next-generation resist systems under investigation (fluorostyrenes, fluoromethacrylates, and siloxane-modified methacrylates). The process has been shown to apply to bilayer and single layer systems, and to develop both positive and negative images.

Several modified polymer systems have emerged from this program which balance the SC CO<sub>2</sub> solubility requirements and imaging characteristics, as the preliminary imaging studies have shown. The use of SC CO<sub>2</sub> developing will have significant positive impact on the current levels of waste generation, and the process meets the requirements of an environmentally responsible method. As image feature size is reduced over the next ten years, it is certain that SC CO<sub>2</sub> developing will offer advantages over liquid developing by minimizing problems with swelling and resist pattern collapse, and will prove to be an efficient and cost effective method for processing photoresists.

The CO<sub>2</sub> pressure and temperature requirements for dissolving most of the polymers tested are very reasonable with respect to supercritical fluid processes. The range of suitable CO<sub>2</sub> developing conditions defined on this program increases the flexibility of the process; the same piece of equipment can be used to develop a wide range of resist systems by simple adjustment of temperature and pressure.

Implementation of SC CO<sub>2</sub> developing in semiconductor manufacturing operations is certain to place users in a strategic position in the global marketplace, and promises to be a useful and versatile process for application to advanced photoresist systems well into the 21st century.

## **9.0 RECOMMENDATIONS**

The successful results generated on this program and the potential merits of SC CO<sub>2</sub> developing of next-generation photoresists indicate that the technology should receive further investigation. Potential users of SC CO<sub>2</sub> developing including IBM have expressed interest in the early results and are enthusiastic about continued efforts.

There are many facets of the technology which need to be further explored in terms of the developing process itself and its impact on lithographic operations and semiconductor manufacture. A Phase II program would address the process and equipment requirements for full commercialization of SC CO<sub>2</sub> developing. Some suggested areas of future research include:

**1. Examination of a broad range of polymer and copolymer systems.** Polymer modification is a straight forward approach to tailoring solubility properties and imaging characteristics, and to maintaining synergy between the two. Chemical structure, composition, molecular weight, and glass transition temperature are among the properties of polymers which influence solubility, optical properties such as transparency and absorbance, and sensitivity to radiation. It would be advantageous to demonstrate the applicability of SC CO<sub>2</sub> developing to a diversity of resist systems.

**2. Investigation of SC CO<sub>2</sub> developing conditions.** Process optimization requires that the "most suitable" conditions are utilized which give the best results for any given system, and simultaneously, the economics must justify the use of the process. Based on the results of Phase I, a wide range of process conditions were found to satisfy solubility requirements for a number of resist systems, which suggests that the process is quite versatile. It is important to delineate an optimum range of conditions over which a variety of resists can be developed in order to extend process latitude, flexibility, and applicability.

**3. Determination of exposure dose/CO<sub>2</sub> solubility relationships.** Definition of required exposure dose to induce sufficient chemical change of the exposed resist is an important task for every resist system. The required exposure dose must render insoluble (for negative imaging) or soluble (for positive imaging) the exposed areas of the resist; with SC CO<sub>2</sub> the developing conditions are adjustable parameters for influencing solubility. Thus, unlike liquid developing, the SC CO<sub>2</sub> process has two variables (exposure dose and developing conditions) that must be balanced to produce quality images. The relationship between these variables requires further investigation in order to predict, in a manner similar to contrast curves, the contrast and resolution of the images.

**4. Investigation of photoresist formulations.** There are many types of additives that are used in resist formulations to enhance the performance of the system. For example, surfactants are often added to improve the adhesion of the polymer to the substrate, sensitizers are usually required to increase the resist's sensitivity to radiation, and depending on the chemistry of the resist, additives such as photoacid generators or cross-linking promoters are essential to the chemical mechanism. It will be necessary to determine if the SC CO<sub>2</sub> developing process or the use of the modified polymers will influence formulation requirements. Can traditional formulation additives still be used? Will they even be necessary? Will performance and economics be positively impacted by adjustments in formulation requirements? These are

among the many questions that will need to be addressed in order to commercialize the SC CO<sub>2</sub> developing process.

**5. Examination of the impact of SC CO<sub>2</sub> developing on pre- and post-developing resist processing.** There are numerous processing steps currently required between the spin-coating step and the exposure step, and between exposure and developing. For example, the coated wafers are often baked before and after exposure. After developing, the system may require etching (for bilayer and multilayer resists). It will be important to examine how the SC CO<sub>2</sub> developing process will effect these other processes and, ultimately, the overall economics.

**6. Demonstration of imaging capabilities.** This will be the critical step in proceeding with commercialization of SC CO<sub>2</sub> developing. After determining that the polymer systems of interest exhibit appropriate solubility and imaging characteristics, it is essential to show that high quality, sub-half micron images can be produced. It has already been shown on Phase I that SC CO<sub>2</sub> developing offers the necessary selectivity to produce images with some polymer systems, but it is crucial to demonstrate that the quality and integrity of the images are not compromised at the small scale.

**7. Comparison of SC CO<sub>2</sub> and liquid developing.** Ultimately, the commercial potential of SC CO<sub>2</sub> developing will lie in its effectiveness compared to conventional liquid methods. Environmental acceptability will not be enough to generate commercial interest; comparative or superior image quality must additionally be demonstrated. There are many technical and economic advantages to using SC CO<sub>2</sub> developing, not only waste minimization and process versatility, but as feature size is increasingly reduced, problems such as swelling and resist pattern collapse will not be encountered. A more quantitative comparison of SC CO<sub>2</sub> developing with liquid methods will point out the technical and economic benefits of the "dry" process.

**8. Generation of prototype equipment.** A small SC CO<sub>2</sub> developing unit will demonstrate to potential users the simplicity of the process operation and the ease with which it can be integrated into manufacturing operations. Although the scope of work required on a Phase II program may limit the amount of funding that can be applied to building a prototype unit, it is expected that successful completion of a Phase II effort will prove to potential users the viability of the SC CO<sub>2</sub> developing process and will lead to Phase III commitment.

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